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(54) Title: HYDROGENATION PROCESS

(57) Abstract: A hydrocarbon hydrogenation process and a catalytic composition having hydrogenation functionality. The catalytic composition includes at least two noble metals supported on an inorganic, porous crystalline phase support material having pores with diameters of at least about 13 Angstrom Units and exhibiting, after calcination, an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Å with a relative intensity of 100, and having a benzene sorption capacity greater than about 15 grams benzene per 100 grams of the support material at 50 torr and 25°C. The noble metals are selected from the group consisting of Pd, Pt, Rh and Ir and the crystalline material is a metallosilicate or an aluminosilicate. The hydrocarbon hydrogenation process includes contacting a hydrocarbon feedstock containing aromatics, olefins, or aromatics and olefins with the catalytic composition under superatmospheric conditions; wherein the concentration of the aromatics, olefins or aromatics and olefins in the product is reduced.

HYDROGENATION PROCESS

BACKGROUND OF INVENTION

The present invention relates to hydrogenation catalysts and their use in a hydrogenation process. In particular, the present invention relates to the hydrogenation of very low aromatic diesel fuels and other hydrocarbon streams.

Hydrogenation is adding one or more hydrogen atoms to an unsaturated hydrocarbon (e.g., an olefin or aromatic compound). Hydrogenation may occur either as direct addition of hydrogen to the double bonds of unsaturated molecules, resulting in a saturated product, or it may cause breaking of the bonds of organic compounds, with subsequent reaction of hydrogen with the molecular fragments. Examples of the first type (called addition hydrogenation) are the conversion of aromatics to cycloparaffins and the hydrogenation of unsaturated vegetable oils to solid fats by addition of hydrogen to their double bonds. Examples of the second type (called hydrogenolysis or hydrocracking) are cracking of petroleum and hydrogenolysis of coal to hydrocarbon fuels.

The benefits of "purifying" petroleum fractions through hydrogen processing have been known since the early 1930's. However, because of a lack of cheap hydrogen and the high pressures formerly required, the process did not develop commercially until the middle 1950's. The advent of catalytic reforming, which made inexpensive hydrogen-rich off-gas available, encouraged hydrogen-processing development. Subsequent advances in catalyst technology allowed operating pressure requirements to be reduced. Today, hydrogenation is a well-established process both in the chemical and petroleum refining industries and is used extensively to prepare reformer feedstock and to some extent for catalytic cracking feedstock preparation. Product upgrading of middle distillates, cracked fractions, lube oils, gasolines, and waxes by means of hydrogen treating is also widespread. Severity of treatment depends largely upon feedstock properties and the required improvement. Cracked stocks and heavy materials call for severe conditions.

Hydrogen treating is often justified for reasons other than the production of superior fuels. Hydrogenation improves yields; substantially eliminates waste-disposal problems caused by mercaptans, phenols, and thiophenols; and reduces corrosion problems from sulfur, cyanides and organic acids. Hydrogen treating also is important in sulfur recovery and subsequent reduction of air pollution by sulfur acid gases.

Hydrogenation is conventionally carried out in the presence of a catalyst which usually comprises a metal hydrogenation component on a porous support material, such as a natural clay or a synthetic oxide. Nickel is often used as a hydrogenation component, as are noble metals such as platinum, palladium, rhodium and iridium. Typical support materials include kieselguhr, alumina, silica and silica-alumina. Depending upon the ease with which the feed may be hydrogenated, the hydrogen pressures used may vary from quite low to very high values, typically from about 100 to 2,500 psig.

A variety of organic compounds can be hydrogenated easily in the presence of a catalyst. Catalytic hydrogenation of olefins can be carried out either in gas or in liquid phase, depending on their molecular weights. A nickel-containing catalyst and sometimes platinum or palladium catalysts are employed. Aromatic compounds may be reduced either in the vapor phase at atmospheric pressure or in the liquid phase at hydrogen pressures up to 200 atmospheres (2×10^4 kilopascals). In the latter case, aromatics, such as benzene, toluene, and p-cymene, can be hydrogenated readily in the presence of a nickel catalyst. In the case of naphthalene or substituted naphthalenes, the product may be the tetra- or decahydronaphthalenes derivative.

Hydrogenation is an exothermic process and is generally favored thermodynamically by lower temperatures and by higher H_2 partial pressures. However, for practical reasons, moderately elevated temperatures are normally used and for petroleum refining processes, temperatures in the range of 100° to 700°F are typical. Hydrogenative treatment is frequently used in petroleum refining to improve the qualities of lubricating oils, both of natural and synthetic origin. Hydrogenation, or hydrotreating, is used to reduce residual unsaturation in the lubricating oil, and to remove heteroatom-containing impurities and color

bodies. The removal of impurities and color bodies is of particular significance for mineral oils which have been subjected to hydrocracking or catalytic dewaxing. For both hydroprocessed mineral and synthetic stocks, the saturation of lube boiling range olefins is a major objective.

The extensive use of hydrogenation catalysts in the chemical and petroleum industries for a variety of applications has led to a need for more active catalysts and catalysts which are more sulfur and/or nitrogen tolerant so that they can be used for longer periods between regeneration or replacement. More active hydrogenation catalysts increase the efficiency of a process and enable smaller reactor beds to be used. In addition, operating costs can be reduced by using hydrogenation catalysts which are more sulfur and/or nitrogen tolerant.

SUMMARY OF THE INVENTION

In accordance with the present invention, a catalytic composition having hydrogenation functionality and a hydrocarbon hydrogenation process are provided. The catalytic composition includes at least two noble metals which are supported on a support material that includes an inorganic, porous crystalline phase material exhibiting, after calcination, an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Å with a relative intensity of 100, and having a benzene sorption capacity greater than about 15 grams benzene per 100 grams of the anhydrous crystal at 50 torr and 25°C. The noble metals preferably make up at least 0.1 weight percent of the catalytic composition. The preferred noble metals are selected from the group consisting of Pd, Pt, Rh and Ir, and are bound in a refractory inorganic oxide that is selected from alumina, silica, silica-alumina, titania, zirconia, magnesia or combinations thereof. The preferred crystalline material is a metallosilicate or an aluminosilicate.

In one embodiment, the crystalline phase material of the catalytic composition has, after calcination, a hexagonal arrangement of uniformly sized pores with diameters of at least about 13 Å and a hexagonal electron diffraction pattern that can be indexed with a d_{100} value

greater than about 18 Angstrom Units. In a preferred embodiment, the crystalline phase material exhibits an electron diffraction pattern, following calcination, that can be indexed with a d_{100} value greater than about 18 Angstrom Units and with at least one peak whose d-spacing corresponds to the d_{100} value from the electron diffraction pattern. The crystalline phase material exhibits a benzene adsorption capacity of greater than about 15 grams benzene per 100 grams of the crystalline phase material at 50 torr and 25 °C.

The crystalline phase material of the catalytic composition has a composition expressed as follows:

$$M_{n/q}(W_a X_b Y_c Z_d O_h) \qquad (1)$$

wherein M is one or more ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; W is one or more divalent elements; X is one or more trivalent elements; Y is one or more tetravalent elements; Z is one or more pentavalent elements; a, b, c, and d are mole fractions of W, X, Y, and Z, respectively; h is a number of from 1 to 2.5; and $(a + b + c + d) = 1$. In a preferred embodiment, W includes a divalent first row transition metal or magnesium; X includes aluminum, boron, gallium or iron; Y includes silicon or germanium; and Z includes phosphorus. In another preferred embodiment, a and d are 0 and $h = 2$.

In another embodiment, the crystalline phase material is a composition of matter that includes an inorganic, porous crystalline phase material exhibiting, after calcination, an X-ray diffraction pattern having values substantially as shown below:

d-spacing, d_n Å	d_n/d_1	relative intensity
$d_1 \geq 18$	1.0	100
$d_1 - d_2$	0.87 ± 0.06	w - m

The preferred support material is M41S and the preferred catalysts are PtPd/M41S and PtPd/MCM-41.

The hydrocarbon hydrogenation process includes contacting a hydrocarbon feedstock containing aromatics, olefins, or aromatics and olefins with the catalytic composition under superatmospheric conditions; wherein the concentration of the aromatics, olefins or aromatics and olefins in the product is reduced. In preferred embodiments, the feedstock is a diesel fuel range or a jet fuel range hydrocarbon.

The hydrogenation catalysts of the present invention are more active than those previously used while being more sulfur and nitrogen tolerant. Moreover, the hydrogenation catalysts of the present invention provide increased efficiency and reduce operating costs.

BRIEF DESCRIPTION OF THE FIGURES

Other objects and many attendant features of this invention will be readily appreciated as the invention becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

FIG. 1 is a graph comparing the hydrogenation activity of the hydrogenation catalyst of the present invention for sweet aromatic feeds.

FIG. 2 is a graph comparing the hydrogenation activity of the hydrogenation catalyst of the present invention for sour aromatic feeds.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, highly active hydrogenation catalysts, which are more sulfur and/or nitrogen tolerant, are used in the production of low-aromatics diesel production and other hydrogenation processes. The hydrogenation catalysts contain a hydrogenation

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component that includes combination noble metal on a support having an inorganic, porous crystalline phase material. Crystalline support materials which may be used in the hydrogenation catalyst include the M41S group of mesoporous crystalline materials, which is described in U.S. Patent No. 5,102,643 and is exemplified by, but not limited to, the MCM-41 and MCM-48 materials. MCM-41, which is described in U.S. Patent No. 5,098,684, is characterized by a microstructure with a uniform, hexagonal arrangement of pores with diameters of at least about 1.3 nm. The preferred catalytic form of this material is the aluminosilicate, although other metallosilicates may also be utilized. MCM-48 has a cubic structure and is described in U.S. Patents Nos. 5,102,643 and 5,198,203; both of which, along with U.S. 5,098,684, are incorporated herein in their entirety by reference. U.S. Patent No. 5,573,657 to Degnan et al. discloses hydrogenation catalysts having similar support materials and is incorporated herein by reference in its entirety.

The hydrogenation catalysts are particularly useful for distillate hydrogenation. However, many other hydrogenation processes can take the advantage of these high activity catalyst. For example, hydrogenation of polyalpha-olefin (PAO) for synthetic lubricant base stock production is particularly attractive since pore size of the support material can be varied widely to accommodate the relatively bulky molecules of the lubricant base stock. In addition, hydrogenation of vegetable oils and white oil hydrogenation are other examples of bulky molecules that can be processed. The catalysts of the present invention can also be used for the hydrogenation of smaller molecules, such as benzene hydrogenation or aromatic hydrogenation of sweet feed in the second-stage of a hydrocracker.

A preferred catalyst of the present invention includes a combination PtPd metal component and a MCM-41 support material. The PtPd/MCM-41 catalyst can also produce high-quality jet and diesel fuels, saturate polynuclear aromatics ("PNAs"), and reduce the adverse effects by the PNAs. Some PNAs are known or suspected to be carcinogenic, or to have some other type of undesirable biological characteristics.

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Hydrogenation Catalyst

The catalytic material used in the present invention includes a novel synthetic composition of matter which includes an ultra-large pore size crystalline phase as a support for the metal component of the catalyst. This material is an inorganic, porous crystalline phase material which can be characterized (in its calcined form) by an X-ray diffraction pattern having at least one peak at a d-spacing greater than about 18 Angstrom Units (Å) with a relative intensity of 100. The crystalline phase material has a benzene sorption capacity of greater than 15 grams of benzene per 100 grams of the material at 50 torr and 25°C. The preferred form of the crystalline material is an inorganic, porous material having a hexagonal arrangement of uniformly-sized pores with a maximum perpendicular cross-section pore dimension of at least about 13 Å, and typically within the range of from about 13 Å to about 200 Å. A preferred form of this hexagonal crystalline composition, identified as MCM-41, has the characteristic structure of hexagonally-arranged, uniformly-sized pores of at least 13 Å diameter. The crystalline phase material exhibits a hexagonal electron diffraction pattern that can be indexed with a d_{100} value greater than about 18 Å, which corresponds to at least one peak in the X-ray diffraction pattern. This material is described in detail in U.S. Pat. No. 5,098,684 to Kresge et al.

The inorganic mesoporous crystalline material used as a component of the catalyst has the following composition:

$$M_{n/q} (W_a X_b Y_c Z_d O_h) \tag{1}$$

wherein W is a divalent element, such as a divalent first row transition metal, e.g. manganese, cobalt and iron, and/or magnesium, preferably cobalt; X is a trivalent element, such as aluminum, boron, iron and/or gallium, preferably aluminum; Y is a tetravalent element such as silicon and/or germanium, preferably silicon; Z is a pentavalent element, such as phosphorus; M is one or more ions, such as, for example, ammonium, Group IA, IIA and VIIB ions, usually hydrogen, sodium and/or fluoride ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the

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number of moles or mole fraction of M; a, b, c, and d are mole fractions of W, X, Y and Z, respectively; h is a number of from 1 to 2.5; and $(a + b + c + d) = 1$.

In a preferred embodiment of the crystalline material defined by equation (1), $(a + b + c)$ is greater than d, and $h = 2$. In another preferred embodiment a and $d = 0$, and $h = 2$. The preferred materials for use in making the present catalysts are the aluminosilicates although other metallosilicates may also be used.

In the as-synthesized form, the support material has a composition, on an anhydrous basis, expressed empirically as follows:

$$rRM_{n/q} (W_a X_b Y_c Z_d O_h) \qquad (2)$$

where R is the total organic material not included in M as an ion, and r is the coefficient for R, i.e., the number of moles or mole fraction of R.

The M and R components are associated with the material as a result of their presence during crystallization, and are easily removed or, in the case of M, replaced by post-crystallization methods described below.

To the extent desired, the original M, e.g. sodium or chloride, ions of the as-synthesized material of this invention can be replaced in accordance with conventional ion-exchange techniques. Preferred replacing ions include metal ions, hydrogen ions, hydrogen precursor, e.g. ammonium, ions and mixtures of these ions. Particularly preferred ions are those which provide the desired metal functionality in the final catalyst. These include hydrogen, rare earth metals and metals of Groups VIIA (e.g. Mn), VIIIA (e.g. Ni), IB (e.g. Cu), IVB (e.g. Sn) of the Periodic Table of the Elements and mixtures of these ions.

The crystalline (i.e., having sufficient order to provide a diffraction pattern such as, for example, by X-ray, electron or neutron diffraction, following calcination with at least one peak) mesoporous material may be characterized by its structure, which includes extremely

large pore windows, as well as by its high sorption capacity. The term "mesoporous" is used here to indicate crystals having uniform pores within the range of from about 13Å to about 200 Å. The mesoporous materials have uniform pores within the range of from about 13 Å to about 200 Å, more usually from about 15 Å to about 100Å. Since these pores are significantly larger than those of other crystalline materials, it is appropriate to refer to them as ultra-large pore size materials. For the purposes of this application, a working definition of "porous" is a material that adsorbs at least 1 gram of a small molecule, such as Ar, N_2, n-hexane or cyclohexane, per 100 grams of the solid.

The catalytic material can be distinguished from other porous inorganic solids by the regularity of its large open pores, whose pore size more nearly resembles that of amorphous or paracrystalline materials, but whose regular arrangement and uniformity of size (pore size distribution within a single phase of, for example, ±25%, usually ±15% or less of the average pore size of that phase) resemble more those of crystalline framework materials such as zeolites. The preferred materials have a hexagonal arrangement of large open channels that can be synthesized with open internal diameters from about 13 Å to about 200 Å. The term "hexagonal" is intended to encompass not only materials that exhibit mathematically perfect hexagonal symmetry within the limits of experimental measurement, but also those with significant observable deviations from that ideal state. A working definition as applied to the microstructure of the present invention would be that most channels in the material are surrounded by six nearest neighbor channels at roughly the same distance. Defects and imperfections will cause significant numbers of channels to violate this criterion to varying degrees, depending on the quality of the material's preparation. Samples which exhibit as much as ±25% random deviation from the average repeat distance between adjacent channels still clearly give recognizable images of the present ultra-large pore materials. Comparable variations are also observed in the d_{100} values from the electron diffraction patterns.

The most regular preparations of the support material give an X-ray diffraction pattern with a few distinct maxima in the extreme low angle region. The positions of these peaks approximately fit the positions of the hkO reflections from a hexagonal lattice. The X-ray diffraction pattern, however, is not always a sufficient indicator of the presence of these

materials, as the degree of regularity in the microstructure and the extent of repetition of the structure within individual particles affect the number of peaks that will be observed. Indeed, preparations with only one distinct peak in the low angle region of the X-ray diffraction pattern have been found to contain substantial amounts of the material in them. Other techniques to illustrate the microstructure of this material are transmission electron microscopy and electron diffraction. Properly oriented specimens of the material show a hexagonal arrangement of large channels and the corresponding electron diffraction pattern gives an approximately hexagonal arrangement of diffraction maxima. The d_{100} spacing of the electron diffraction patterns is the distance between adjacent spots on the hkO projection of the hexagonal lattice and is related to the repeat distance a_0 between channels observed in the electron micrographs through the formula $d_{100} = a_0 \sqrt{3/2}$. This d_{100} spacing observed in the electron diffraction patterns corresponds to the d-spacing of a low angle peak in the X-ray diffraction pattern of the material. The most highly ordered preparations of the material obtained so far have 20-40 distinct spots observable in the electron diffraction patterns. These patterns can be indexed with the hexagonal hkO subset of unique reflections of 100, 110, 200, 210, etc., and their symmetry-related reflections.

In its calcined form, the crystalline material may be further characterized by an X-ray diffraction pattern with at least one peak at a position greater than about 18 Angstrom Units d-spacing (4.909° 2θ for Cu K-alpha radiation) which corresponds to the d_{100} value of the electron diffraction pattern of the material, and an equilibrium benzene adsorption capacity of greater than about 15 grams benzene /100 grams crystal at 50 torr and 25 °C (basis: crystal material having been treated in an attempt to insure no pore blockage by incidental contaminants, if necessary).

The equilibrium benzene adsorption capacity characteristic of this material is measured on the basis of no pore blockage by incidental contaminants. For instance, the sorption test will be conducted on the crystalline material phase having any pore blockage contaminants and water removed by ordinary methods. Water may be removed by dehydration techniques, e.g. thermal treatment. Pore blocking inorganic amorphous materials, e.g. silica, and organics may be removed by contact with acid or base or other

chemical agents such that the detrital material will be removed without detrimental effect on the crystal.

More particularly, the calcined crystalline non-layered material may be characterized by an X-ray diffraction pattern with at least two peaks at positions greater than about 10 Å d-spacing (8.842 $^\circ\theta$ for Cu K-alpha radiation), at least one of which is at a position greater than about 18 Å d-spacing, and no peaks at positions less than about 10 Å d-spacing with relative intensity greater than about 20% of the strongest peak. Still more particularly, the X-ray diffraction pattern of the calcined material of this invention will have no peaks at positions less than about 10 Å d-spacing with relative intensity greater than about 10% of the strongest peak. In any event, at least one peak in the X-ray diffraction pattern will have a d-spacing that corresponds to the d_{100} value of the electron diffraction pattern of the material.

The equilibrium benzene adsorption capacity is determined by contacting the material of the invention, after dehydration or calcination at, for example, about 540°C. for at least about one hour and other treatment, if necessary, in an attempt to remove any pore blocking contaminants, at 25°C. and 50 torr benzene until equilibrium is reached. The weight of benzene sorbed is then determined.

The ammonium form of the catalytic material may be readily converted to the hydrogen form by thermal treatment (calcination). This thermal treatment is generally performed by heating one of these forms at a temperature of at least 400°C. for at least 1 minute and generally not longer than 20 hours, preferably from about 1 to about 10 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience, such as in air, nitrogen, ammonia, etc. The thermal treatment can be performed at a temperature up to about 750°C. The thermally treated product is particularly useful in the catalysis of certain hydrocarbon conversion reactions and it is preferred that the material should be in this from for use in the present catalysts.

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Catalyst Metal Component

The hydrogenation catalyst includes a metal as the hydrogenation component. The hydrogenation component is provided by a combination of metals. Noble metals of Group VIII, especially palladium, platinum, rhodium and iridium can be used. For certain applications, where sulfur and other contaminants such as phosphorus are in low concentrations in the feedstock, e.g. sulfur or phosphorous <10 ppm, a combination of palladium and platinum is preferred. In addition to the synergistic benefit which a combination of platinum and palladium provides with respect to hydrogenation activity, the palladium metal provides resistance to nitrogen poisoning.

The content of the metal component will vary according to its catalytic activity. Thus, the highly active noble metals may be used in smaller amounts. The present support materials for the metal component are notable in that they are capable of including a greater proportion of metal than previous support materials because of their extraordinarily large surface area. The metal component may exceed about 30 percent in a monolayer. The hydrogenation component can be exchanged onto the support material, impregnated into it or physically admixed with it. If the metal is to be impregnated into or exchanged onto the mesoporous support, it may be done, for example, by treating the zeolite with a palladium or platinum metal-containing ion. Suitable platinum compounds include chloroplatinic acid, platinous chloride and various compounds containing the platinum amine complex. The metal compounds may be either compounds in which the metal is present in the cation of the compound and compounds in which it is present in the anion of the compound. Both types of compounds can be used. Palladium or platinum compounds in which the metal is in the form of a cation of cationic complex, e.g., $Pd(NH_3)_4Cl_2$ or $Pt(NH_3)_4Cl_2$ are particularly useful, as are other anionic complexes such as the nitrate, vanadate and metatungstate ions. Cationic forms of other metals are also very useful since they may be exchanged onto the crystalline material or impregnated into it.

Hydrotreating

The catalysts of the present invention can be used in a variety of hydrotreating processes. For aromatic feedstocks, the temperature of the hydrotreating step is from about

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200° to 850° F (about 93° to 454° C), preferably about 300° to 750° F. (about 150° to 400°

C), with the exact selection dependent on the desulfurization desired for a given feed and

catalyst. Because the hydrogenation reactions which take place are exothermic, a rise in

temperature takes place along an adiabatic reactor. A temperature rise of about 20° to 200° F

(about 11° to 111° C) is typical under most hydrotreating conditions.

Since the feeds are readily desulfurized, low to moderate pressures may be used for

hydrogenation, typically from about 50 to 1500 psig (about 445 to 10443 kPa), preferably

about 300 to 1000 psig (about 2170 to 7,000 kPa). Pressures are total system pressure,

reactor inlet. Pressure will normally be chosen to maintain the desired aging rate for the

catalyst in use. The space velocity (hydrodesulfurization step) is typically about 0.5 to 10

LHSV (liquid hourly space velocity, hr⁻¹), preferably about 1 to 6 LHSV (hr⁻¹). The hydrogen

to hydrocarbon ratio in the feed is typically about 500 to 5000 SCF/Bbl (about 90 to 900

n.l.l⁻¹), usually about 1000 to 2500 SCF/B (about 180 to 445 n.l.l⁻¹). The extent of the

desulfurization for feed pretreatment will depend on the initial feed sulfur content and, of

course, on the product sulfur specification with the reaction parameters selected accordingly.

EXAMPLE 1

The Pt/Pd on MCM-41 catalyst, which is one of the preferred catalysts, can be

prepared as follows. MCM-41 powder and Versal 300 Alumina powder are mulled for 5

minutes. Water is added to obtain a total 40 wt% solids content and the mixture is further

mulled for another 15 minutes. The mixture is extruded through a 1/20" quadrulobe die and

dried at 250°F overnight. The dried extrudates are calcined at 1000°F in air using 5 cm³ air /

min / cm³ extrudate for a period up to 12 hours. The calcined extrudates are drained of excess

solution and washed with 10 volumes de-ionized or distilled water / volume extrudate

followed by overnight drying at 250°F. After drying, the extrudates are calcined at 1000°F

in air using 5 cm³ air / min / cm³ extrudate over a period of 3 hours.

The extrudates are co-impregnated to a 0.3 wt% Pt / 0.5 wt% Pd loading in a rotary

vessel equipped with a spray nozzle, using a Pt-tetraammine-nitrate and Pd-tetraammine-

nitrate solution equivalent to the extrudate incipient wetness volume. The extrudates are then

dried overnight at 250°F and calcined at 680°F in air using 5 cm³ air / min / cm³ extrudate for a period of 1 hour. Properties of the catalyst are given in Table 1.

TABLE 1

CATALYST PROPERTIES

PROPERTY	VALUE
Platinum Content	0.32 wt%
Paladium Content	0.54 wt%
Surface Area	527 m²/gm
Pore Volume	1.027 cm³/gm

The final calcined catalyst used in the present invention includes a hydrogenation component containing at least two noble metals. Prior to pretreatment in the reactor, these metals can be present in the catalyst in their elemental form or as their oxides, sulfides, or mixtures thereof. In a preferred embodiment, palladium and platinum are used. The palladium and platinum are present in an amount ranging from about 0.1 percent by weight to about 2.0 percent by weight, preferably from about 0.2 percent by weight to about 1.5 percent by weight, and more preferably from about 0.3 percent by weight to about 1.2 percent by weight based on the total weight of the catalyst and calculated as oxide, for best results. Catalyst metals concentrations outside of these total metals content ranges have been found to be less efficient.

The weight ratio of elemental palladium to elemental platinum generally ranges from about 10:1 to 1:10, preferably from about 8:1 to 1:2, and more preferably from about 5:1 to 1:1 for best results. It has been found that these ratio ranges provide the most effective hydrogenation.

Several methods known to those skilled in the art can be used for either deposing or incorporating the hydrogenation component on the support using heat-decomposable salts of the noble metals. For example, platinum and palladium can be impregnated onto the support separately, or can be co-impregnated onto the support using various aqueous impregnation

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solutions, including, but not limited to, chloroplatinic acid, palladium chloride, tetraammine palladium chloride, and tetraammine platinum chloride.

EXAMPLE 2

The Pt/Pd on MCM-41 catalyst prepared in Example 1 was tested against a reference catalyst. A commercial PtPd catalyst supported on an aluminum-bound zeolite and having a high heat of wetting and a high surface area (greater than 220 m^2/g) was used as the reference catalyst. Both catalysts were evaluated using the same procedure. Both catalysts were dried at 500°F for 3 hours under a flow of nitrogen stream in a fixed-bed pilot unit. After the drying, both catalysts were activated by hydrogen at 300°F and 500°F for 4 hours, each. The evaluation was conducted at 350-600°F, 1.3 LHSV, 700 psig, and 4000 scf/b of once-through hydrogen circulation rate.

A commercial diesel-range distillate was used as the feed stock. This feed is preferred as the "sweet feed" since it is almost free of sulfur (3 ppmw S) and nitrogen (<0.5 ppmw N). In order to test the resistance (or tolerance) of the catalysts to sulfur and nitrogen poisoning, the sweet feed was doped with dibutyldisulfide and t-butylamine to 30 ppmw S and 10 ppmw N, respectively to create a "sour feed." The properties of the sweet feed and sour feed are shown below in Table 2.

TABLE 2
FEED PROPERTIES

PROPERTY	SWEET FEED	SOUR FEED
Gravity, °API	23.70	23.70
Hydrogen, wt%	11.93	11.93
Sulfur, ppmw	4	26
Nitrogen, ppmw	<0.50	10
Aromatics, wt%	46.80	46.80
Distillation (D2887), °F		
IBP	394.5	—

10%	463.9	—
50%	534.2	—
90%	615.0	—
EBP	731.3	—

Figure 1 shows the test results for the sweet feedstock using the PtPd/MCM-41 catalyst of the present invention and the reference catalyst. The graph of the Remaining Aromatics in the sweet feed by weight versus Temperature shows that the PtPd/MCM-41 catalyst is significantly more active than the reference catalyst for hydrogenating the sweet feed. The PtPd/MCM-41 catalyst achieved complete aromatic saturation at a temperature greater than 450°F, while the reference catalyst never achieved complete hydrogenation for the temperature range evaluated.

Figure 2 shows the test results for the sour feedstock using the PtPd/MCM-41 catalyst and the reference catalyst. The graph of the Remaining Aromatics in the sweet feed by weight versus Temperature shows that the PtPd/MCM-41 catalyst was more resistant (or tolerant) to the poisoning by nitrogen and sulfur than the reference catalyst. It is known that noble metal-containing catalysts are sensitive to nitrogen and sulfur-containing compounds and, therefore, in order for a hydrogenation catalyst to be effective, it must exhibit a tolerance to these compounds. As shown in Figure 2, the PtPd/MCM-41 catalyst achieved the complete hydrogenation of the sour feedstock at temperatures greater than 550°F, but the reference catalyst did not achieve complete hydrogenation.

Thus, while there have been described the preferred embodiments of the present invention, those skilled in the art will realize that other embodiments can be made without departing from the spirit of the invention, and it is intended to include all such further modifications and changes as come within the true scope of the claims set forth herein.

CLAIMS:

1.   A hydrocarbon hydrogenation process comprising contacting a hydrocarbon feedstock containing aromatics, olefins, or aromatics and olefins with a catalyst under superatmospheric conditions; wherein the concentration of said aromatics, olefins or aromatics and olefins in the product is reduced; and wherein said catalyst comprises two noble metals and is supported on a support material comprising an inorganic, porous crystalline phase material having pores with diameters of at least about 13 Angstrom Units and exhibiting, after calcination, an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Å with a relative intensity of 100, and having a benzene sorption capacity greater than about 15 grams benzene per 100 grams of said material at 50 torr and 25 °C.

2.   The hydrocarbon hydrogenation process according to claim 1, wherein said noble metals are selected from the group consisting of Pd, Pt, Rh and Ir.

3.   The hydrocarbon hydrogenation process according to claim 1, wherein said crystalline material is a metallosilicate or an aluminosilicate.

4.   The hydrocarbon hydrogenation process according to claim 1, wherein said catalytic composition includes at least 0.1 weight percent of said noble metals.

5.   The hydrocarbon hydrogenation process according to claim 1, wherein said crystalline phase material exhibits, after calcination, a hexagonal arrangement of uniformly sized pores with diameters of at least about 13 Å and a hexagonal electron diffraction pattern that can be indexed with a d_{100} value greater than about 18 Angstrom Units.

6.   The hydrocarbon hydrogenation process according to claim 2, wherein said crystalline phase material has an X-ray diffraction pattern following calcination with at least one peak whose d-spacing corresponds to the d_{100} value from the electron diffraction pattern.

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7.   The hydrocarbon hydrogenation process according to claim 2, wherein said noble metals are bound in a refractory inorganic oxide, wherein said refractory inorganic oxide is selected from the group consisting of alumina, silica, silica-alumina, titania, zirconia, magnesia and combinations thereof.

8.   The hydrocarbon hydrogenation process according to claim 1, wherein said feedstock is a diesel fuel boiling range hydrocarbon and said support material is M41S.

9.   The hydrocarbon hydrogenation process according to claim 1, wherein said catalyst is PtPd/M41S or PtPd/MCM-41.

10.   The hydrocarbon hydrogenation process according to claim 1, wherein said feedstock is a jet or diesel fuel boiling range hydrocarbon.

Figure 1
Hydrogenation Activity: Sweet Feed
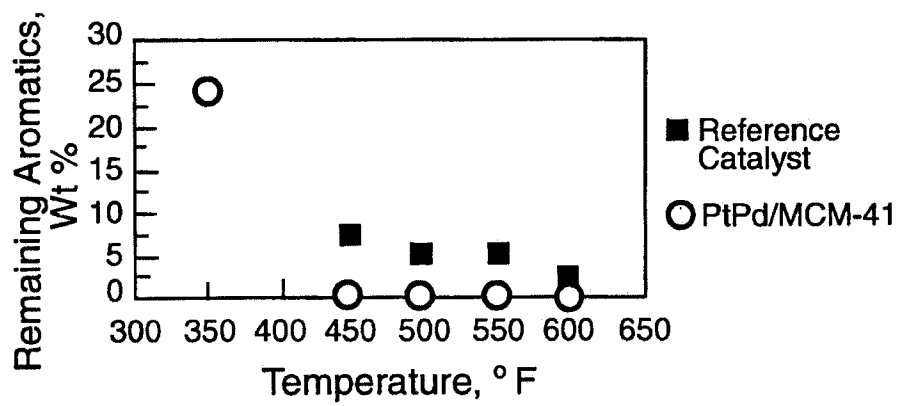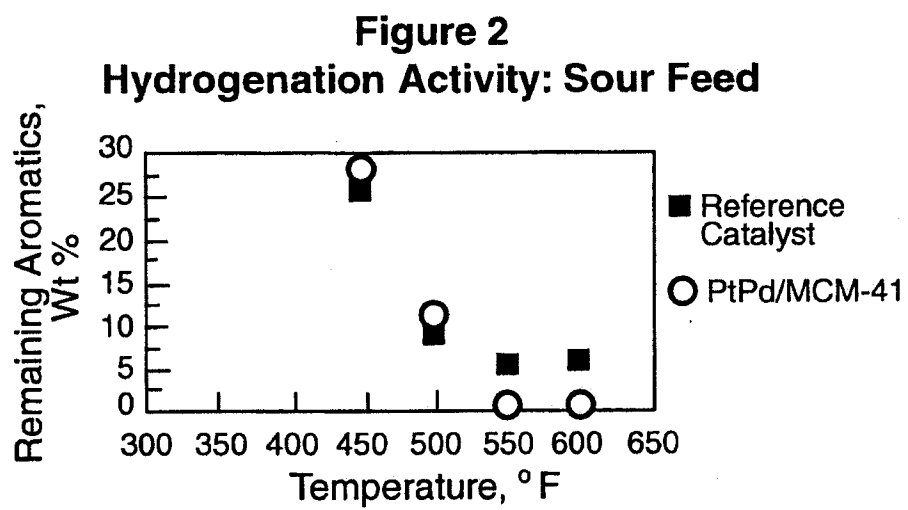
Figure 2
Hydrogenation Activity: Sour Feed

INTERNATIONAL SEARCH REPORT

A.   CLASSIFICATION OF SUBJECT MATTER

IPC(7)   :C10G 45/00, 45/44, 45/52, 45/54; C07C 7/163, 5/03, 5/10
US CL   :208/143, 144; 585/258, 259, 260, 266, 269, 273

According to International Patent Classification (IPC) or to both national classification and IPC

B.   FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/143, 144; 585/258, 259, 260, 266, 269, 273

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST search terms: hydrogenation, MCM-41, M41S, noble metal

C.   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,451,312 A (APELIAN et al) 19 September 1995 (19-09-95), see col. 2, line 41 through col. 3, line 15; col. 4, lines 18-49; col. 6, lines 45-56; col. 8, lines 24-61; col. 9, line 4 through col. 10, line 31; and the examples.	1-10

☐   Further documents are listed in the continuation of Box C.   ☐   See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 OCTOBER 2000	08 JAN 2001

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